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Superconducting phases of URu_2Si_2

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Thermodynamic data near the superconducting T_c on several different single-crystal specimens of the heavy-fermion system URu_2Si_2 are presented. Multiple-peak structure and narrow transition widths ($\Delta T_c/T_c = 0.05$) are observed in the specific heat of the highest-quality samples. By carefully sectioning one of the crystals, it is shown that these peaks occur in macroscopically different parts of the crystal, and not as a result of vector superconductivity. Implications for the multiple-peak structure in UPt_3 are discussed.

The superconducting (SC) state in the heavy-fermion (HF) compound[1] UPt_3 is commonly believed to be described by a vector order parameter instead of the usual BCS *s*-wave state. Evidence for this comes from a variety of sources, including the known importance of spin fluctuations for electronic coupling,[2] the power-law behaviors in ultrasonic attenuation[3] and specific heat[4] below T_c and, most recently, the observation of multiple-peak structure[4,5] (MPS) in the specific heat $C(T)$ at T_c in high-quality samples possessing a large electronic mean free path. The MPS in particular has been the subject of numerous recent studies,[6-13] these driven by the *prima facie* similarity, at least in zero magnetic field, to the *A-B* vector superfluid-superfluid transition in ^{3}He. These studies have been focused mainly on determining the phase diagram for the MPS with ever higher precision, using both bulk and microscopic probes. Equally important for MPS, however, is the effect of modification of the electronic properties, e.g., by atomic substitution and, *a fortiori*, by observation of MPS in other HF SC materials.

This paper describes efforts to observe MPS in the HF SC (Refs. 14-16) URu_2Si_2. This material is similar to UPt_3 in that (1) it exhibits an antiferromagnetic (AF) transition with a small ordered moment[17] ($\sim 10^{-2}\mu_B/U$) persisting into the SC state, (2) the SC T_c of both materials is ~ 1 K, and (3) power-law behavior is observed[16] in $C(T)$ below T_c. Also, like UPt_3, earlier specimens of URu_2Si_2 studied had broad $C(T)$ anomalies at T_c, giving the possibility of hidden MPS. In the present work we show that, indeed, the highest-quality single-crystal samples exhibit sharp MPS in $C(T)$. However, we will show that the MPS does not originate from vector superconductivity, but rather from different phases occurring in distinct regions of the crystal. In one specimen, there is an isolated transition at $T_c = 0.8$ K and no evidence for MPS is seen at a noise level 1/50 of the signal in UPt_3. These results are in accord with symmetry constraints and the known magnetic structure of URu_2Si_2.

URu_2Si_2 (tetragonal $ThCr_2Si_2$ structure) was the first HF compound known to possess both SC ($T_c \sim 1$ K) and magnetic order.[14-16] Accompanying the AF transition at 17.5 K is a spin-density-wave (SDW) anomaly in the resistivity and a large reduction in the specific-heat coefficient γ, from 180 to 60 mJ/mol K^2. the magnetic properties have been extensively studied by neutron and magnetic x-ray scattering.[17-19] The magnetic order is ferromagnetic (FM) within basal plane sheets and AF between sheets of easy *c*-axis, Ising-like uranium spins, with a total ordered moment of only $(0.03 \pm 0.01)\mu_B$. For comparison, UPt_3 has $T_c = 0.5$ K, an AF transition at 5 K, an ordered moment of $0.03\mu_B$, and a spin configuration which is AF in the basal plane, with a symmetry lower than that of the hexagonal lattice. The influence of the AF symmetry on the SC order parameter has been discussed as a possible cause of the MPS in UPt_3.

The goal of the present study was to improve the crystal quality for the SC properties and therefore a number of crystal-growth runs were carried out. The URu_2Si_2 samples we report on were all single crystals grown by the "tri-arc" Czochralski growth method.[20] Samples A and C were grown at the University of Amsterdam and sample B was grown at McMaster University (see Table I). Other growth batches were examined and found to possess either broad SC specific-heat peaks ($\Delta T_c/T_c > 0.15$) or weak FM transitions[21] at 35 K, and were thus deemed unsuitable for the present study. The samples reported here were structurally refined by single-crystal x-ray diffraction, with the results summarized in Table I. Measurements of dc magnetization (M) were obtained with a commercial magnetometer, ac susceptibility (χ_{ac}) with a mutual inductance method at 1 kHz, resistance (R) with a standard four-probe ac technique, and specific heat (C) using a semiadiabatic method.

The overall quality (low impurity and defect levels) of

TABLE I. Crystal parameters.

Sample	T_c (K)	a (Å)	c (Å)	RRR
A	1.10	4.1293(1)	9.5749(2)	27
B	0.76,0.98	4.1277(3)	9.5746(7)	25
C (as grown)	0.83,0.96,1.29	...	...	...
C (interior)	0.83	4.1292(1)	9.5744(2)	16

the URu_2Si_2 samples is indicated by several different measures. First, the lattice parameters agree well with those of the best prior determinations, and there is little variation from sample to sample (see Table I). Second, the stoichiometry of Ru and Si relative to U, as computed from the diffraction peak heights, is within 2% of the ideal 1:2:2 composition in all three samples. Third, the residual-resistance ratio (RRR), a coarse indicator of impurity concentration, was measured between 300 and 0 K (using a T^2 extrapolation) (Table I). The SDW at T_N reduces the RRR by creating a gap over $\frac{2}{3}$ of the Fermi surface —nevertheless, RRR values in excess of 20, generally considered high for intermetallics, were found. This compares reasonably well with samples of UPt_3 exhibiting MPS, where RRR$\sim$200 without an SDW anomaly. The ultimate measure of quality, however, is the sharpness of the $C(T)$ jump at T_c, which provides a good measure of the electronic homogeneity, and is the quantity of most interest. This will be discussed in detail below.

In Fig. 1 is shown the specific heat versus temperature as C/T vs T in ascending order of sample quality, as evidenced by the sharpness of the rise in T_c. For sample A, $T_c=1.10$ K and has a width (10%–90%) in C/T of $\Delta T_c/T_c=0.12T_c$. A large transition width in a high-quality single crystal such as this is most likely a result of the extreme sensitivity of a vector SC order parameter to time-reversal invariant defects.[22] Regardless of the dimensionality of the order parameter, T_c is a fixed quantity for a particular compound. It is surprising, therefore, that in sample B, two distinct transitions are observed, at 0.76 and 0.98 K, each with a width approximately the same as sample A. In sample C (as grown), yet a different result is found. Here, there is an extremely sharp anomaly at 0.81 K and a weaker one[23] at 1.3 K. The multiplicity of T_c's is unusual, but more surprising is the narrowness of the lowest-temperature peak; this indicates a T_c modification mechanism different from simple random-impurity-induced pair breaking, since such an effect would simultaneously broaden and lower T_c. This result suggests that each transition is associated with a distinct crystalline state.

While peaks in $C(T)$ indicate the bulk nature of the various phases, diamagnetic steps in $\chi_{ac}(T)$ can yield information on the spatial configuration of these phases. For sample A, as shown in Fig. 1, the single broad transition is reflected in a single diamagnetic step in $\chi_{ac}(T)$, consistent with the view of inhomogeneous broadening on a *microscopic* length scale ($\ll\delta$, the skin depth of the excitation field). The behavior of $\chi_{ac}(T)$ for the other samples is qualitatively different. For samples B and C (as grown), the MPS in $C(T)$ is reflected in multiple steps in $\chi_{ac}(T)$. These steps constitute strong evidence for phase

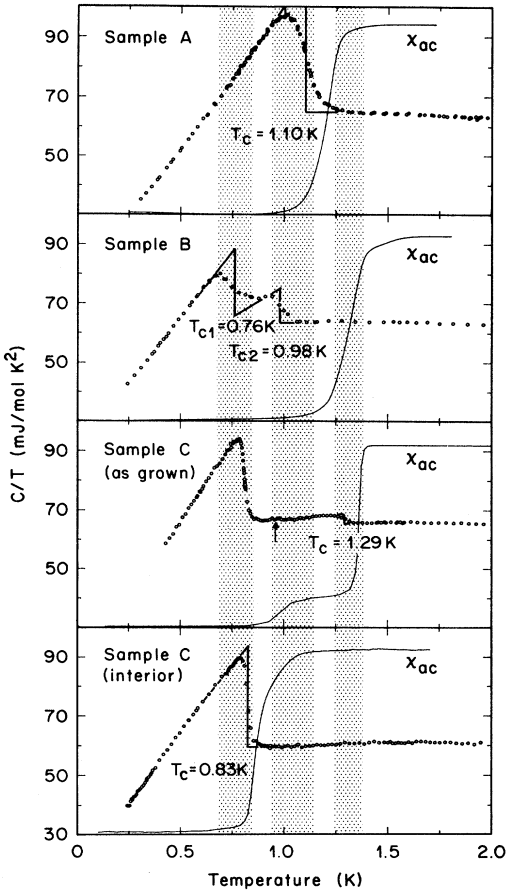

FIG. 1. Specific heat C divided by temperature T, plotted against T for the various URu_2Si_2 samples. Also shown as solid lines are the shielding current, measured by ac susceptibility χ_{ac} in arbitrary units. The solid lines drawn through the C/T data are equal-area constructions used for determining T_c. The arrow locates a weak maximum in C/T indicating a possible third SC phase in sample C (as grown). The shaded regions represent approximately the three distinct temperatures at which superconductivity is observed in URu_2Si_2.

separation on a *macroscopic* length scale ($\simeq\delta$). We note that multiple steps are not a necessary consequence of macroscopic phase separation. Rather, they indicate that neither of the phases dominates the shielding signal by virtue of either having a large demagnetization factor or by topologically enclosing the sample. In fact, this geometrical factor is evident in the magnitude of the upper transition in sample C (as grown), which is caused by less than 10% of the total sample [as determined from the entropies of the two major $C(T)$ peaks]. We tested the idea that the higher-T_c phase of sample C was dominating the signal by a geometrical effect by removing a center section of the sample using multiple cuts with a string saw. The results are shown in the bottom frame of Fig 1. We find that the entire upper transition of sample C was removed in the sectioning process. Because the remaining peak occurs at the same temperature as does the lower transition of sample B, we conclude that sample B must also consist of macroscopically segregated material. [The

small size (40 mg) of this particular sample, however, precluded a sectioning procedure as used for sample C.] Most importantly, however, the lattice parameters of sample C (interior) (T_c=0.81 K) are found to be identical within experimental error to those of sample A (T_c=1.1 K).

The main result of this work can be summarized as follows. URu_2Si_2 material, which nominally displays *multiple* T_c's, does so because it contains *spatially separated regions* of *structurally indistinguishable* material, each with a *single* T_c. Usually when multiphase behavior is observed in a physical property it is possible to distinguish different crystal phases either by structural or chemical diagnostic methods. It is easy, however, to see how T_c can vary dramatically among different URu_2Si_2 samples which, as mentioned earlier, are structurally and stoichiometrically indistinguishable. Modifications involving either hydrostatic pressure or atomic substitution show T_c to be highly sensitive to small perturbations. For the pressure effect, since[24] dT_c/dP=0.13 K/kbar, and the bulk modulus[25] $B\sim 3\times 10^3$ kbar, a 0.3-K shift in T_c, as observed between samples A and C (interior), is accompanied by a volume change of $\Delta V/V\sim 8\times 10^{-4}$ and, assuming isotropic compression, lattice-constant changes of only $\sim 2.5\times 10^{-4}$. For a substitution effect, though no small-impurity-concentration studies exist for URu_2Si_2, a similar T_c change, 0.3 K, can be expected only at the 0.5% impurity level, based on doping studies of the HF SC compounds $CeCu_2Si_2$,[26] and UPt_3.[27] These estimated modulation levels for both pressure (strain) and substitutional impurity effects are either at or below the best detection levels. It is clear, then, that materials with vastly *different* SC T_c's can *appear* to be both structurally and chemically *identical*.

Determination of the precise difference between the materials exhibiting different T_c's is beyond the scope of the present investigation. It is not unreasonable, however, to presume that the different phases possess different defect superstructures, a common feature of ternary silicides.[28] These superlattices could be driven by a small off stoichiometry (at the level discussed above) which is produced by loss of Si during crystal growth. The different phases will then be related at the microscopic level by a different strain or electron density and will in turn effect T_c through a coupling constant or density-of-states modification. In this general scenario for MPS, the qualitative nature (e.g., symmetry) of the SC state is expected to be the same for each of the different T_c phases if the defect structures are qualitatively similar. This is supported by H_{c2} measurements on sample C (as grown) which show the upper and lower transitions following trajectories differing only by a scale factor (Fig. 2). [H_{c2} in both c-axis and basal-plane directions was measured for sample C (interior) and excellent agreement was found with the results of Ref. 14.]

A *large* multiplicity of superlattices, as postulated here for URu_2Si_2, is not expected to occur in UPt_3, and in fact among the many UPt_3 samples studied by other workers,[4,5,11] there seems to be only a set of two T_c's, converging at the values 0.45 and 0.50 K for the best samples. In addition, compared to URu_2Si_2, the H_{c2} behavior is qualitatively different, displaying two intersecting phase boundaries (four lines meeting at a single H-T value).[12,13] It seems very likely that the origin of MPS is different for UPt_3 than for URu_2Si_2. This difference might be fundamental—in particular, it has been espoused that MPS in UPt_3 is due to a rotation of the SC order parameter.[29,30] In this scenario, UPt_3 is electronically homogeneous on a length scale greater than the coherence length. The present results suggest an alternative (and more conservative) explanation for the difference in H_{c2} behavior, namely, a subtle type of phase separation. If this occurs in UPt_3, then different phases might have different U:Pt ratios which after annealing would be manifested in different basal-plane symmetries, SC states and hence $H_{c2}(T)$ behavior.

Finally, we examine the sharpness of the $C(T)$ jump at T_c for sample C (interior). In Fig. 3 is shown $C(T)$ data in reduced units for both this sample and for UPt_3 after Fisher *et al.*[5] The sharpness of these peaks suggests a simple measure for the observability of a second peak, the "step area," A, defined as the product of the T_c difference

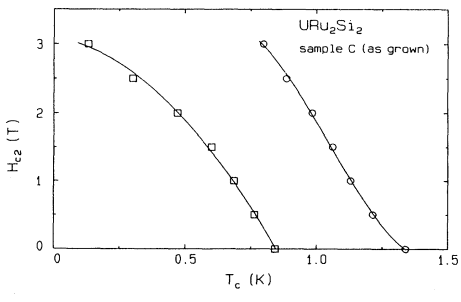

FIG. 2. Upper critical field H_{c2} of URu_2Si_2 (sample C, as grown), as determined by the midpoint of the shielding transition in ac susceptibility. The applied field is at approximately 45° with respect to the c axis. The two sets of data correspond to the two transitions observed in the specific-heat measurements of Fig. 1. The solid lines are to guide the eye.

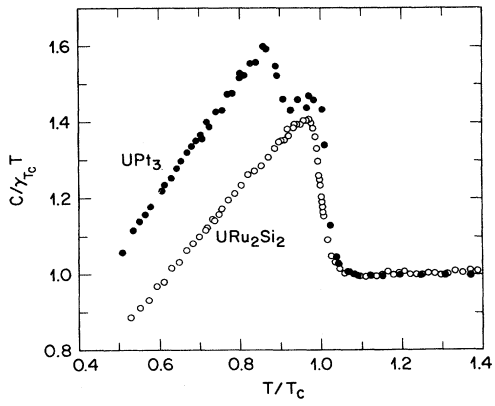

FIG. 3. Specific heat C divided by $\gamma(T_c)T$, plotted against T/T_c for UPt_3, after Fisher *et al.* (Ref. 5) and for URu_2Si_2 (sample C, this work). Although the transition widths, as measured by the slope on the high-temperature side of the peak, are comparable, there is no sign of a double transition in URu_2Si_2.

$\delta T_c/T_c$, and the height of the lower peak above the upper one, $\delta C/T_\gamma(T_c)$. For the UPt_3 data of Fisher *et al.*, $A(UPt_3)=\delta T_c \delta C/[\gamma(T_c)T_c^2]=1.5\times10^{-2}$. For URu_2Si_2 sample C (interior), we can place an upper limit of $A(URu_2Si_2)\lesssim 7.5\times10^{-4}$ on the presence of a second transition, a factor of 50 smaller than the UPt_3 signal. We note that a single transition is consistent with current intrinsic explanations of MPS in UPt_3. There the splitting is held to be caused by a rotation of the SC order parameter induced by a symmetry-breaking field of possible magnetic origin.[29,30] Such a field must have a lower symmetry than the crystal lattice and it has been proposed that the weak magnetic order observed in UPt_3 is the source of this field.[31,32] In URu_2Si_2, the magnetic symmetry is not lower than that of the crystal, unlike UPt_3, and splitting of the SC transition would not be expected within this scenario.[32,33]

Note added. After this work was completed, we learned of a similar study by Maple *et al.*[34] in which MPS was also observed in URu_2Si_2. No attempt, however, was made in that work to separate physically the different phases.

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